

Reaction Kinetics of Cluster Impurities

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We study the kinetics of clustered immobile reactants in diffusion-controlled single-species annihilation. We consider the initial conditions where the immobile reactants occupy a subspace of dimension d_i , while the rest of the d -dimensional space is occupied by identical mobile particles. The Smoluchowski rate theory suggests that the immobile reactants concentration, $s(t)$, exhibits interesting behavior as a function of the codimension, $\bar{d} \equiv d - d_i$. This survival probability undergoes a survival-to-extinction transition at $\bar{d}_c = 2$. For $\bar{d} < \bar{d}_c$, a finite fraction of the immobile reactants survives, while for $\bar{d} \geq \bar{d}_c$, $s(t)$ decays indefinitely. The corresponding asymptotic properties of the concentration are discussed. The theoretical predictions are verified by numerical simulations in 2D and 3D.

P.A.C.S. Numbers: 02.50.-r, 05.40.+j, 82.20.-w, 82.20.Wt

I. INTRODUCTION

The kinetics of diffusion-controlled reactions have attracted much interest recently. Despite their simplicity, the underlying stochastic processes show complex nonequilibrium behavior. For homogeneous reaction processes, substantial theoretical knowledge is available [1–5, 7–10]. For reaction processes such as single-species annihilation [7] and single-species aggregation [10], it is well known that for $d \leq 2$ spatial correlations are important in the long time limit, while for $d > 2$ such correlations are negligible asymptotically.

A recent generalization of the annihilation process $A + A \rightarrow 0$ to situations where the reactants have different mobilities was shown to exhibit a rich array of asymptotic behavior. Such a process is well suited for describing reactions that involve particles of different sizes. The case where a small number of particles move according to one diffusion coefficient and the rest of the particles according to another is especially interesting because of its simplicity. The survival probability of a single “impurity” particle in a background of identical particles, $s(t)$, depends in a nonuniversal fashion on the diffusivity of the impurity. In one dimension, the results are especially intriguing. While for the aggregation process, a mapping to a random walk in three dimension enables an exact solution [11], for the annihilation process only an approximate theory is available [12]. The survival probability of a single immobile impurity particle is equivalent to the fraction of unvisited sites by annihilating random walkers [13]. Additionally, as the annihilation process is equivalent to the $T = 0$ Ising model with Glauber dynamics [14], $s(t)$ equals the fraction of “cold” spins, *i. e.*, the number of spins that did not flip up to time t . Numerically, time-dependent and finite size simulations [12, 15, 16], exact enumerations [17], as well as time power-series studies [12] suggest that the impurity survival probability depends algebraically on time, $s(t) \sim t^{-\alpha}$, with a non-trivial exponent, $\alpha \cong 0.375$, while the corresponding exponent for the aggregation case, $A + A \rightarrow A$, is $\alpha = 1$. A recent theoretical work confirmed that the exact value is indeed $\alpha = 3/8$ [18]. In addition, for tri-

molecular annihilation, $A + A + A \rightarrow 0$, it was found that the impurity decays faster than a power-law but slower than an exponential $s(t) \sim \exp(-(\ln t)^{3/2})$ [13]. Hence, in one-dimension, the impurity decay kinetics are highly sensitive to the microscopic details of the reaction process.

In this study, we present a generalization of the isolated impurity problem. We restrict our attention to situations where the impurity particles are immobile. We investigate the collective behavior of such immobile impurities by considering initial conditions in which the immobiles are clustered. For simplicity, the immobiles occupy a subspace of dimension d_i embedded in a d -dimensional space. For convenience, we introduce the codimension $\bar{d} = d - d_i$. Note that the case $\bar{d} = d$ corresponds to the single impurity problem. In the long time limit, neighboring immobile reactants “shield” each other, and as a result, the immobile reactants decay significantly slower than the background. The concentration inside the subspace is larger than in the bulk, and consequently, the boundary between the subspace and the bulk acts as an absorbing boundary. The geometry of the system reduces to a \bar{d} -dimensional one. Applying the Smoluchowski rate theory to the mobile particles in dimension d and to the immobile particles in dimension \bar{d} , make theoretical predictions concerning the asymptotic form of the survival probability possible. The survival probability of an immobile reactant undergoes a survival-extinction transition at $\bar{d} = \bar{d}_c = 2$. Below this critical codimension, a finite fraction of the immobiles survive, while at a higher codimension their concentration decays forever. For $\bar{d} = 1$, the approach to the final concentration is an algebraic one, $s(t) - s_\infty \sim t^{-1/2}$ for $d > 2$, with a logarithmic correction at $\bar{d} = 2$, $s(t) - s_\infty \sim t^{-1/2} \ln t$. At the critical codimension, $\bar{d} = 2$, an unusual logarithmic decay occurs $s(t) \sim (\ln t)^{-\alpha(d, \bar{d})}$, while for $\bar{d} > 2$, a dimension dependent decay is found, $s(t) \sim t^{-\alpha(d, \bar{d})}$.

II. THE SINGLE IMPURITY PROBLEM

In this section we review the rate equation theory and apply it to the single impurity problem. This approach truncates the infinite hierarchy of equations describing the concentration at the first order. Above the critical dimension, spatial fluctuations are asymptotically irrelevant and thus, this theory is exact. Moreover, this theory can be extended to arbitrary dimension, and is especially attractive due to its simplicity.

In the lattice version of the homogeneous single-species annihilation process, particles hop independently with rate D to any one of their nearest-neighbor sites. An attempt to land on an occupied site results in the removal of both particles from the system. Symbolically, the process can be written as



Hence, the concentration, $c(t)$, obeys the following rate equation, $dc/dt \propto -c_{AA}$, where c_{AA} is the concentration of pairs of neighboring particles. This approach leads to an infinite hierarchy of equations and is of limited practical use. Alternatively, one assumes that the annihilation rate is proportional to the flux experienced by a particle, $dc/dt \propto -jc$ [1]. This flux can be evaluated by placing an absorbing particle in a diffusing background of concentration c . Since j is proportional to c , the concentration is described by the following rate equation,

$$\frac{dc}{dt} = -kc^2, \quad (2)$$

with k being the d -dimensional reaction rate. Above the critical dimension $d_c = 2$ the reaction rate approaches a constant. Otherwise, the reaction rate is time dependent since the target particle is surrounded by a depletion zone the size of the diffusion length \sqrt{Dt} . In appendix A, we detail a heuristic derivation of the reaction rate in arbitrary dimension using the quasistatic approximation. Asymptotically, the reaction rate is given by

$$k \sim \begin{cases} t^{-1/2} & d = 1; \\ (\ln t)^{-1} & d = 2; \\ 1 & d > 2. \end{cases} \quad (3)$$

By introducing a modified time variable

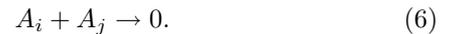
$$z(t) = \int_0^t k(t') dt', \quad (4)$$

the rate equation simplifies, $dc/dz = -c^2$. Without loss of generality, we set the initial concentration to unity and consequently, the concentration $c = 1/(1+z)$ is found. Evaluating the modified time variable, z , we arrive at the following asymptotic behaviors of the homogeneous single-species annihilation process,

$$c(t) \sim \begin{cases} t^{-1/2} & d = 1; \\ t^{-1} \ln t & d = 2; \\ t^{-1} & d > 2. \end{cases} \quad (5)$$

Interestingly, these results are asymptotically exact [8,9], despite the assumptions involved with the rate theory. Moreover, a similar concentration is obtained for the aggregation process $A + A \rightarrow A$ as well. In low dimensions, the reaction proceeds with a slow rate, since particles are effectively repelling each other. On the other hand, in high dimensions spatial correlations are practically irrelevant, and the concentration decays faster. The critical dimension is characterized by typical logarithmic corrections.

The annihilation process can be generalized to heterogeneous situations where the mobilities of the reactants are not equal. Reactants with a diffusion coefficient D_i are denoted by A_i , and the annihilation process can be symbolically written as



Let us consider the special case where a single impurity particle with diffusion coefficient D_i is placed in a uniform background of particles with a diffusion coefficient D . The survival probability of such an impurity particle, denoted by $s(t)$, obeys the generalized rate equation

$$\frac{ds}{dt} = -k_i cs. \quad (7)$$

The reaction process between reactants of diffusivities D and D_i is characterized by the reaction rate k_i , given by (see Appendix)

$$k_i \simeq \begin{cases} K_1(D + D_i)^{-1/2} t^{-1/2} & d = 1; \\ K_2(D + D_i) (\ln((D + D_i)t))^{-1} & d = 2; \\ K_d(D + D_i) & d > 2. \end{cases} \quad (8)$$

Again, it is useful to rewrite the rate equation in terms of the modified time variable z defined by Eq. (4), $ds/dz = -(k_i/k)cs$. Note that in the long time limit the rate ratio approaches a constant that depends only on the diffusion coefficient ratio. By substituting the asymptotic form of the concentration c , $c \sim 1/z$, one finds a purely algebraic dependence of the impurity concentration $s \sim z^{k_i/k}$ for $d \neq 2$ [12]. At the critical dimension, $d = 2$, the leading asymptotic correction to the rate ratio is important, and a detailed calculation is necessary [19]. Using the aforementioned forms of z and k_i , the following impurity concentration is found,

$$s(t) \sim \begin{cases} t^{-\sqrt{\theta}/2} & d = 1; \\ t^{-\theta} (\ln t)^{\theta(1-\ln \theta)} & d = 2; \\ t^{-\theta} & d \geq 2. \end{cases} \quad (9)$$

Hence, the ratio $\theta = (D + D_i)/2D$ governs the long time kinetics. For the case $D_i = 0$, the decay exponent equals $1/\sqrt{8} \cong 0.353$ when $d = 1$, and $1/2$ when $d > 2$. While the latter value is exact, the former is only approximate. Interestingly, this approximate value is quite close to the observed numerical value 0.375 [12,15–17]. However, as this approximation is uncontrolled, its accuracy

can widely vary, and for the exactly soluble aggregation process, the discrepancy in the exponents is larger. To summarize, both in the supercritical regime and in the subcritical regime, the decay of the impurities depends on the diffusivity ratio in a nongeneric fashion.

III. KINETICS OF CLUSTER IMPURITIES

The following questions arise naturally from the above theory: Can the presence of neighboring impurities increase the survival probability of an impurity? If yes, to what extent? To answer these questions we concentrate on the case of immobile reactants, $D_i = 0$. We introduce a generalization of the single immobile impurity problem. Let us consider the initial configuration where the impurities occupy a subspace of dimension d_i . For example, on a simple cubic lattice, the subspace $\{\mathbf{x}|x_1 = \dots = x_{d_i} = 0\}$ is occupied by impurities, with $\mathbf{x} \equiv x_1, \dots, x_d$ the Cartesian coordinates. The rest of the space is occupied by particles with an identical diffusion coefficient D . The annihilation process is the same as Eq. (6). The codimension \bar{d} can be conveniently defined as $\bar{d} = d - d_i$. For example, when $\bar{d} = 1$, the impurities initially occupy a line in 2D, a plane in 3D, *etc.* Figure 1 illustrates the initial configuration for the case $\bar{d} = 1$ in two spatial dimensions. Note also that the single impurity problem corresponds to the special case $\bar{d} = d$.

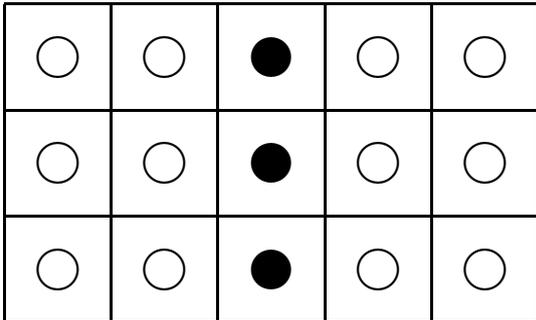


FIG. 1. A line of impurities (bullets) in a two-dimensional background (circles)

Let us consider first a line of impurities in 2D. The presence of nearby static particles can only increase the survival probability of an impurity, and thus, the survival probability is bounded by $s \sim t^{-1/2}$, the corresponding result for the single impurity case for $d \geq 2$. However, the mobile particles decay $c \sim t^{-1}$ is stronger and consequently, the boundary between the mobile reactants and the immobile reactants is equivalent to an absorbing boundary for the mobile reactants. This absorber is not a perfect one since not all sites are occupied with impurities. However, it is well known that in the long time limit a partial absorber is equivalent to a perfect one [20]. A depletion layer of width \sqrt{Dt} develops around the subspace and the mobile reactant concentration profile is

strongly suppressed in this depletion zone. As a result, the geometry of the system is drastically altered. A line in 2D reduces to a one-dimensional geometry. In other words, the codimension becomes the relevant dimension. This simple conclusion has a striking effect on the long time kinetics of the impurities.

One possible way to tackle this problem is to describe this spatial inhomogeneity by the reaction-diffusion equation with proper boundary conditions. However, the leading term in the reaction-diffusion equation is the diffusion term, and this approach is equivalent in the long time limit to the quasistatic approximation, or namely, the Smoluchowsky rate theory. This theory, appealing in its simplicity, leads to new and interesting behaviors for the cluster impurity problem. As discussed above, the relevant dimension is the codimension. Thus, we apply the \bar{d} -dimensional rate equation to the impurity concentration

$$\frac{ds}{dt} = -k_i^{\bar{d}}cs, \quad (10)$$

where $k_i^{\bar{d}}$ is the reaction rate in \bar{d} dimensions. In contrast with the previous analysis, introduction of a modified time variable would not simplify the algebra, since the equations involve different dimensions and consequently, different intrinsic time scales. Instead, the impurity survival probability, $s(t)/s(0)$, is obtained by an integration of the above equation,

$$s(t)/s(0) = \exp\left(-\int_0^t dt' k_i^{\bar{d}}(t')c(t')\right). \quad (11)$$

Since the case $\bar{d} = d$ reduces to the single impurity case (see Eq. (9)), we concentrate on the case $\bar{d} < d$ only. By substituting the proper values of the concentration c in d -dimensions and the reaction rate $k_i^{\bar{d}}$ in \bar{d} -dimensions into Eq. (11), we find the following asymptotic impurity densities,

$$s(t) \sim \begin{cases} s_\infty + \text{const} \times t^{-1/2} \ln t & \bar{d} = 1 \text{ and } d = 2; \\ s_\infty + \text{const} \times t^{-1/2} & \bar{d} = 1 \text{ and } d > 2; \\ (\ln t)^{-K_{\bar{d}}/2K_d} & \bar{d} = 2 \text{ and } d > \bar{d}; \\ t^{-K_{\bar{d}}/2K_d} & \bar{d} > 2 \text{ and } d > \bar{d}. \end{cases} \quad (12)$$

This rich behavior follows directly from the annihilation rate, *i. e.*, the integrand in Eq. (11). If $k_i^{\bar{d}}(t)c(t)$ decays faster than $1/t$, the integral remains finite in the long time limit, and a finite fraction of the impurities survive the annihilation process. Otherwise, all of the impurities eventually annihilate. For $\bar{d} < 2$, this integrand decays faster than $1/t$, while for $\bar{d} \geq 2$, the integrand is dominated by $1/t$. Consequently, the system exhibits a survival-extinction transition at $\bar{d} = 2$. Below this critical codimension, a fraction of the impurities survive, while they decay indefinitely at a higher codimension.

The approach to the final concentration, $s(t) - s_\infty \sim t^{-1/2} \ln t$ for a line in 2D ($\bar{d} = 1$) is reminiscent of the

single impurity decay in 2D. The two cases differ in that s_∞ does not vanish for the cluster case. They also differ in the logarithmic correction. The critical case is characterized by inverse logarithmic decay since the annihilation rate is proportional to $1/(t \ln t) = d \ln(\ln t)/dt$. Both the critical case and the supercritical case follow a power-law with the exponent $\alpha(d, \bar{d}) = K_{\bar{d}}/2K_d$. Thus, both decays depend on the dimension as well as the codimension. Only in the extreme case, $\bar{d} = d$, corresponding to the single impurity case, K_d cancels out and the decay $s \sim t^{-1/2}$ is expected. Generally, a detailed calculation for the dimensionless prefactors K_d is necessary in order to find the various decay exponents. Since the decay in the cluster case $\bar{d} < d$ is slower than in the single impurity case $\bar{d} = d$, we learn that the prefactor K_d is an increasing function of the spatial dimension d . This observation is consistent with the fact that the initial reaction rate is given by $k_i(t=0) = 2(D + D_i)z_d$, with z_d the number of neighboring sites in d -dimensions. Indeed, z_d is an increasing function of d . Above the critical dimension $d = 2$, the effective reaction rate depends weakly on time. Hence, the assumption $K_d \propto z_d$ leads to an approximate value for the decay exponent $\alpha(d, \bar{d}) \cong z_{\bar{d}}/2z_d$. For a simple square lattice one has the $z_d = 2d$ or $\alpha(d, \bar{d}) \cong \bar{d}/2d$. This approximation improves as the dimension and the codimension increase.

The above results can be easily generalized to arbitrary dimensions. Such a generalization is nontrivial only when the temporal nature of the reaction rate is dimension dependent, or namely, below the critical dimension. Using the reaction rates of Eq. (A3), we evaluate the immobile impurity densities,

$$s(t) \sim \begin{cases} t^{-d/2^{1+d/2}} & \bar{d} < 2 \text{ and } d = \bar{d}; \\ s_\infty + \text{const} \times t^{-(d-\bar{d})/2} & \bar{d} < 2 \text{ and } \bar{d} < d < 2; \\ s_\infty + \text{const} \times t^{-(2-\bar{d})/2} \ln t & \bar{d} < 2 \text{ and } d = 2; \\ s_\infty + \text{const} \times t^{-(2-\bar{d})/2} & \bar{d} < 2 \text{ and } d > 2; \\ t^{-1/2} (\ln t)^{(1+\ln 2)/2} & \bar{d} = 2 \text{ and } d = 2; \\ (\ln t)^{-K_{\bar{d}}/2K_d} & \bar{d} = 2 \text{ and } d > \bar{d}; \\ t^{-K_{\bar{d}}/2K_d} & \bar{d} > 2 \text{ and } d \geq \bar{d}. \end{cases} \quad (13)$$

To summarize, a fraction of the impurities survive only when $\bar{d} < 2$ and $d > \bar{d}$. The behavior for $d < 2$ is influenced by the background concentration behavior $c \sim t^{-d/2}$. As a result, the approach towards the limiting concentration is algebraic with a vanishing decay exponent $(d - \bar{d})/2 = d_i/2$ when $\bar{d} \lesssim d < 2$. It will be interesting to see how the above results compare with Renormalization Group studies in the vicinity of the critical codimension $\bar{d} = 2 - \epsilon$.

For completeness, we briefly discuss the early behavior of the system. We consider the case where all lattice sites are initially occupied, such that $c(0) = s(0) = 1$. Following the above discussion, the initial reaction rate is given by $k(t=0) = 2Dz_d$. From Eq. (2), the background concentration is found

$$c(t) \cong (1 + 2Dz_d t)^{-1}, \quad t \rightarrow 0. \quad (14)$$

On the other hand, only interfacial sites contribute to the annihilation of impurities, and as a result $k_i(t=0) = D(z_d - z_{d-\bar{d}})$. By substituting this rate and the early time mobile reactant concentration into Eq. (10), the impurity concentration is calculated in the small time limit,

$$s(t) \cong (1 + 2Dz_d t)^{-\beta(d, \bar{d})}, \quad t \rightarrow 0. \quad (15)$$

The above exponent, $\beta(d, \bar{d})$, equals the reaction rate ratio $\beta(d, \bar{d}) = (z_d - z_{d-\bar{d}})/2z_d$. This exponent should not be regarded as an asymptotic one, since it is relevant only for the short time limit. In addition to the dimension dependence, the early time behavior depends on the lattice structure as well. As the reaction process evolves, such details become irrelevant, and the general asymptotic behavior is recovered. There is no sign of a critical codimension in the early stages since the system is still d -dimensional. After a sufficiently long time, the codimension governs the kinetics.

IV. SIMULATION RESULTS

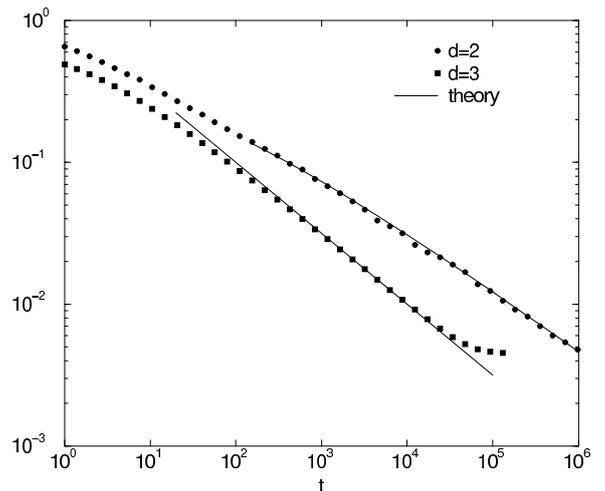


FIG. 2. The impurity concentration $s(t)$ versus t in 2D and 3D. Shown are the case $\bar{d} = 1$ in 2D (bullets) and 3D (squares), and the case $\bar{d} = 2$ in 3D (triangles).

To test the theoretical predictions, we have performed Monte-Carlo simulations for $d = 2$ and 3. The numerical implementation is simple. Initially all L^d sites of the cubic lattice are occupied with reactants, of which $L^{d_i/d}$ are immobile and occupy the subspace $\{\mathbf{x} | x_1 = \dots = x_{d_i} = 0\}$, with the Cartesian coordinates $\mathbf{x} \equiv (x_1, \dots, x_d)$. The rest of the lattice is occupied by identical mobile particles. Periodic boundary conditions are imposed. An elemental simulation step consists of picking a mobile particle at random and moving it to a randomly chosen neighboring site. If this site is occupied, both particles are removed from the system. Time is updated by the

inverse of the total number of mobile particles after each step. The linear dimension of the lattice used in the simulation was $L = 5 \times 10^3$, 2×10^2 in 2D, and 3D respectively. The total number of particles was thus 25×10^6 , and 8×10^6 for 2D, and 3D. In 2D the results represent one realization of the process, while in 3D an average over 10 realizations is taken. Typically, the simulation data are reliable up to time $\propto L^2$ because due to finite size effects.

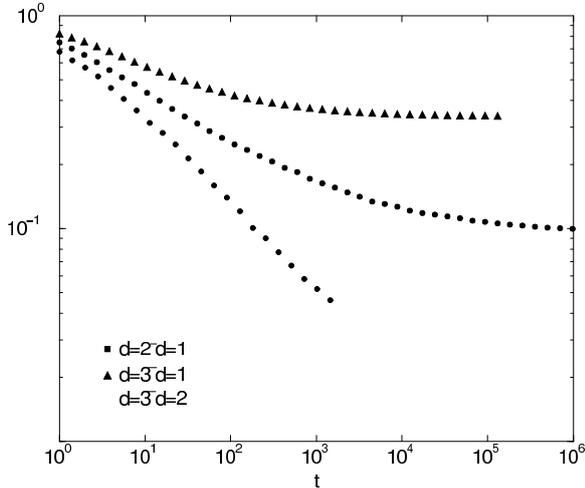


FIG. 3. The quantity $s(t) - s_\infty$ versus time for the case $\bar{d} = 1$. Shown are simulation results in 2D (bullets) and 3D (squares) versus the theoretical prediction of Eq. (12) (solid lines).

We have first verified that the average concentration of the mobile reactants decays according to the well known concentration of Eq. (5). To verify the survival-extinction transition at $\bar{d} = 2$, we measured the impurity concentration versus time (see figure 2). Indeed, for the case $\bar{d} = 1$, $s(t)$ approaches a final nonzero value, s_∞ , while the impurity concentration decays indefinitely for the marginal case, $\bar{d} = 2$. Since the total number of impurities initially present in the latter case is small, we could not verify the inverse logarithmic decay of Eq. (12). For the case $\bar{d} = 1$, we performed a least square fit of the data to the theoretical predictions of Eq. (12). The optimal final concentration was found to be $s_\infty \cong 0.095$ and 0.335 in 2D and 3D, respectively. We verified that similar results occurred for smaller system sizes. In Figure 3, the concentration difference $s(t) - s_\infty$ is plotted versus time. According to the rate theory, this quantity should decay as $t^{-1/2} \ln t$ in 2D, and as $t^{-1/2}$ in 3D. It is seen that the theoretical curves (solid lines) fit well the simulation data in the long time limit. We conclude that the simulation results are consistent with the theoretical predictions.

V. CONCLUSIONS

We have studied the kinetic behavior of clusters of immobile reactants in the single-species annihilation pro-

cess. The codimension, \bar{d} , plays an important role in the long time limit. The Smoluchowsky theory shows that a transition from survival to extinction takes place at $\bar{d} = 2$. For $\bar{d} < 2$, a finite fraction of the impurities survive, while for $\bar{d} \geq 2$ all of the impurities eventually vanish. Furthermore, the asymptotic behavior of the concentration of impurities depends on the dimension as well as the codimension. The theoretical predictions are verified by Monte-Carlo simulations.

This study suggests that the rate theory can be extended to heterogeneous situations. Moreover, a time-dependent reaction equation is equivalent in the long time limit to the detailed reaction-diffusion equation. The success of this theory is remarkable especially considering its simplicity. It will be interesting to apply the same mechanism to more complicated processes, such as multispecies reactions.

VI. ACKNOWLEDGMENTS

I am thankful to P. Krapivsky and S. Redner for useful discussions. This work was supported in part by the MR-SEC Program of the National Science Foundation under Award Number DMR-9400379 and by NSF under Award Number 92-08527.

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APPENDIX A: THE QUASISTATIC APPROXIMATION

The reaction rate, k , can be found by evaluating the flux j experienced by an absorbing test particle of radius R due to a diffusing background of concentration c_0 . Hence, the diffusion equation $\partial c/\partial t = D\nabla^2 c$ is solved under the initial conditions $c|_{t=0} = c_0$ and the absorbing boundary condition $c(r)|_{r=R} = 0$. Although an exact solution can be obtained, we present a simpler approximate technique. Since the length scale governing the diffusion process is \sqrt{Dt} , one assumes that the absorber does not affect the background concentration at distances larger than \sqrt{Dt} . Inside this depletion zone the Laplacian term dominates the spherically symmetric diffusion equation,

$$Dr^{1-d} \frac{\partial}{\partial r} r^{d-1} \frac{\partial c(r)}{\partial r} = 0, \quad R < r < \sqrt{Dt}. \quad (\text{A1})$$

The quasistatic approximation imposes an additional time-dependent boundary condition $c|_{r=\sqrt{Dt}} = c_0$ [21,22]. The concentration profile is readily obtained for $R < r < \sqrt{Dt}$,

$$c(r,t) \simeq \begin{cases} c_0 \left((r/R)^{2-d} - 1 \right) / \left((\sqrt{Dt}/R)^{2-d} - 1 \right) & d < 2; \\ c_0 \ln(r/R) / \ln(\sqrt{Dt}/R) & d = 2; \\ c_0 \left(1 - (r/R)^{2-d} \right) / \left(1 - (\sqrt{Dt}/R)^{2-d} \right) & d > 2. \end{cases} \quad (\text{A2})$$

Above the critical dimension $d_c = 2$, $c(r,t)$ approaches a limiting concentration profile. The reaction rate is given by calculating the total flux seen by the test particle $j = DS_d R^{d-1} \partial c/\partial r$, with S_d the surface area of the d -dimensional unit sphere. We quote the leading asymptotic term of the reaction rate, $k = j/c_0$,

$$k \propto \begin{cases} D^{d/2} t^{d/2-1} & d < 2; \\ D (\ln Dt)^{-1} & d = 2; \\ DR^{d-2} & d > 2. \end{cases} \quad (\text{A3})$$

In the case where the target diffusivity D_T is nonzero, the appropriate diffusion constant is $D + D_T$. We derived the continuum rates, however, the lattice counterparts can be conveniently obtained by setting $R \equiv 1$.